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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 220/22, D06M 15/277	A1	(11) International Publication Number: WO 94/24179 (43) International Publication Date: 27 October 1994 (27.10.94)
(21) International Application Number: PCT/US94/03434		(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 7 April 1994 (07.04.94)		
(30) Priority Data: 08/048,350 14 April 1993 (14.04.93) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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(54) Title: WATER- AND OIL-REPELLENT FLUORO(METH)ACRYLATE COPOLYMERS**(57) Abstract**

Lower homologue perfluoroalkylethyl (meth)acrylates copolymerized with vinylidene chloride and alkyl (meth)acrylates; optionally with N-methylol-acrylamide, hydroxyalkyl (meth)acrylates, and/or alkyloxy (meth)acrylates, impart high levels of water-, alcohol- and oil-repellency to fabrics under mild conditions.

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TITLE

Water- and Oil-Repellent Fluoro(Meth)acrylate Copolymers

FIELD OF THE INVENTION

The invention described herein relates to novel copolymers

- 5 comprising polymer units derived from perfluoroalkylethyl
(meth)acrylates, vinylidene chloride, and alkyl(meth)acrylates which, in
the form of aqueous compositions, will impart oil-, alcohol- and water-
repellency to fabrics without the need to utilize heat-curing of the treated
substrate as practiced in the prior art. (In all instances herein, the term
10 "(meth)acrylate" is used to denote either acrylate or methacrylate, and the
term "N-methylol(meth)acrylamide" is used to denote either N-
methylolacrylamide or N-methylolmethacrylamide.

BACKGROUND OF THE INVENTION

- Perfluoroalkylethyl (meth)acrylate-containing copolymers
15 having utility as textile-treating agents for the purpose of imparting oil-
and water-repellency are known. Solvent-based formulations which do not
require a heat-curing step during application have been described by
Kirimoto and Hayashi in U.S. 3,920,614; however, environmental and
safety concerns now require virtually all such applications to be made from
20 aqueous formulations in place of organic solvents. Greenwood, Lore, and
Rao, in U.S. Patent No. 4,742,140, disclose perfluoroalkylethyl
acrylate/vinylidene chloride/ alkyl (meth)acrylate copolymers which, after
application to polyamide textile substrates from an aqueous formulation,
imparted oil- and water-repellency to the substrates. The Greenwood et
25 al. perfluoroalkylethyl acrylate monomers have the formula:



in which the monomer molecular weight distribution is given as:

- 0-10 weight % of the fluoromonomer with k = or > 4
45-75 weight % of the fluoromonomer with k = 6
30 20-40 weight % of the fluoromonomer with k = 8
1-20 weight % of the fluoromonomer with k = 10
0-5 weight % of the fluoromonomer with k = or > 12

All of the prior compositions which can be applied from an aqueous
emulsion require a heat-curing step after application and drying. For
example, Greenwood et al. heat-treated the fabric at 140°C to 190°C for at
least 30 sec, typically 60 to 180 sec.

SUMMARY OF THE INVENTION

The present invention relates to novel aqueous emulsion polymers based on lower homologue distributions of perfluoroalkylethyl (meth)acrylates copolymerized with vinylidene chloride and
5 nonfluorinated alkyl (meth)acrylates; optionally with N-methylol(meth)acrylamide, hydroxyalkyl (meth)acrylates, and/or alkyloxy (meth)acrylates. It relates also to the use of the copolymers as oil-, water- and alcohol-repellents. The copolymers impart high levels of water-, alcohol- and oil-repellency to fabrics under milder drying and curing
10 conditions than those required to achieve commercially useful repellent properties with conventional aqueous fabric treatment compositions. The aqueous dispersions can be used to treat a variety of woven and nonwoven textile fabrics made from natural or synthetic fibers including cotton, cellulose, wool, silk, polyamide, polyester, polyolefin, polyacrylonitrile, 15 rayon, acetate as well as paper and leather substrates.

DETAILED DESCRIPTION OF THE INVENTION

The perfluoroalkylethyl (meth)acrylates useful for preparing the novel copolymers of this invention are in the form of mixtures of monomers having the formula:

20 $\text{CF}_3\text{CF}_2(\text{CF}_2)_k\text{CH}_2\text{CH}_2\text{OC(O)C(R)=CH}_2$
wherein R = H or CH₃, and k is 4,6,8,10 and 12 consisting essentially of:
25-70 weight % of monomers wherein k = 4 or less
20-40 weight % of monomers wherein k = 6
5-25 weight % of monomers wherein k = 8
25 0-15 weight % of monomers wherein k = 10 or greater.

In a particular embodiment (hereinafter "low distribution"), the distribution is essentially as follows:

30 45-70 weight % of monomers wherein k = 4 or less
20-35 weight % of monomers wherein k = 6
5-10 weight % of monomers wherein k = 8
0-5 weight % of monomers wherein k = 10 or greater;

In another particular embodiment (hereinafter "middle distribution"), the distribution consists essentially of:

35 25-45 weight % of monomers wherein k = 4 or less
25-40 weight % of monomers wherein k = 6
10-25 weight % of monomers wherein k = 8
1-15 weight % of monomers wherein k = 10 or greater.

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Because of their industrial availability, fluoropolymers of this invention which are based on the "middle distribution" are considered to be the best mode of carrying out the invention, particularly the fluoropolymer of EXAMPLE 6.

- 5 The nonfluorinated (meth)acrylates comprise alkyl (meth)acrylates in which the alkyl group is a straight or branched chain radical containing 2 to 20 carbon atoms, preferably 8 to 18 carbon atoms. The C₂-C₂₀ alkyl (meth)acrylates (linear or branched) are exemplified by, but not limited to, alkyl(meth)acrylates where the alkyl group is ethyl, propyl, butyl, isoamyl, hexyl, cyclohexyl, octyl, 2-ethylhexyl, decyl, isodecyl, lauryl, cetyl, or stearyl. The preferred examples are 2-ethylhexyl acrylate, lauryl acrylate and stearyl acrylate. Optional N-methylol monomers are exemplified by, but not limited to N-methylolacrylamide and N-methylolmethacrylamide. The optional hydroxyalkyl (meth)acrylates have alkyl chain lengths in range between 2 and 4 carbon atoms, and are exemplified by 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate. The optional alkyloxy(meth)acrylates also have alkyl chain lengths in range between 2 and 4 carbon atoms, and contain between 1 and 12 oxyalkylene units per molecule, preferably between 4 and 10 oxyalkylene units per molecule, and most preferably between 6 and 8 oxyalkylene units per molecule, as determined by gas chromatography/mass spectrometry. Specific examples of the poly(oxyalkylene)-(meth)acrylates are exemplified by, but not limited to, the reaction product of 2-hydroxyethyl methacrylate and nine mols of ethylene oxide (also known as 2-hydroxyethyl methacrylate/9-ethylene oxide adduct) and the reaction product of 2-hydroxyethyl methacrylate and six mols of ethylene oxide (also known as 2-hydroxyethyl methacrylate/6-ethylene oxide adduct). In an embodiment, the copolymers are made from 50-80 wt. % perfluoroalkylethyl (meth)acrylates, 10-40 wt. % C₂-C₂₀ alkyl (meth)acrylates, 10-40 wt. % vinylidene chloride, 0-2 wt. % N-methylol-acrylamide, 0-2 wt. % 2-hydroxyethyl methacrylate and 0-5 wt. % poly(oxyethylene)methacrylate.
- 10 15 20 25 30

- The fluorinated copolymers of this invention are prepared in water by free radical initiated emulsion polymerization of a mixture of perfluoroalkylethyl (meth)acrylate homologues with vinylidene chloride, alkyl (meth)acrylates, and, optionally, N-methylol(meth)acrylamide and hydroxyalkyl- or alkyloxy-(meth)acrylates. The fluoropolymers of this
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invention are made by agitating the monomers described above in water with a surfactant in a suitable reaction vessel which is equipped with an agitation device and an external heating and cooling device. A free radical initiator is added and the temperature raised to 40-70°C. A
5 polymerization regulator or chain transfer agent may be added to control molecular weight of the resultant polymer. The product of the reaction is an aqueous dispersion which is diluted further with water. The polymerization initiator is exemplified by, but not limited to, 2,2'-azobis(2-amidinopropane) dihydrochloride or 2,2'-azobis(isobutyramidine)
10 dihydrochloride. The polymerization regulator or chain transfer agent is exemplified by, but not limited to, dodecylmercaptan.

The fluoropolymers of this invention will impart oil- and water- repellency to fibrous substrates, such as textile fabrics, without heating the treated substrate above room temperature (about 20°C).
15 Thus, the fluoropolymers can be applied to the substrate in the form of an aqueous emulsion by conventional techniques, such as padding or spraying, after which excess liquid is squeezed off or removed by vacuum. After removal of excess liquid, development of the water- and oil-repellency characteristics of the substrate can be achieved simply by air-drying the treated substrates. The period of time required to effect air-drying will be apparent to one skilled in the art by observation. As would be expected, the time needed to complete air-drying of the treated substrate will vary, depending on a number of factors, such as the composition and weight of the substrate, the quantity of liquid retained by
20 the substrate at the time air-drying is commenced, and the like. While heating is not necessary for development of the repellent properties of the polymers of this invention, the treated fabric may be warmed for a matter of seconds so as to speed up the completion of air-drying. In one embodiment, the treated fabric was air-dried for about 16 to 24 hours at
25 about 20°C; in another, about 72 hours at about the same temperature. In yet another embodiment, the treated fabric was air-dried for about 16 to 24 hours at about 20°C, and thereafter heated at about 38°C for about 10 seconds.

In the Examples that follow, further illustrating the
35 invention, the terms "perfluoroalkylethyl acrylate mixture A" and "perfluoroalkylethyl acrylate mixture B" refer respectively to mixtures of

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perfluoroalkylethyl acrylates having the "low distribution" and the "middle distribution" described above.

EXAMPLE 1

A water emulsion was prepared by mixing the following:

- 5 64.0 g of perfluoroalkylethyl acrylate mixture A
 18.0 g stearyl methacrylate
 8.0 g stearic acid/14-ethylene oxide adduct
 2.0 g 2-hydroxyethyl methacrylate/9-ethylene oxide adduct
 1.0 g N-methylolacrylamide
10 1.0 g 2-hydroxyethyl methacrylate
 0.5 g dodecylmercaptan
 140.0 g deionized water.

The emulsion was added to a glass reaction vessel equipped with an agitator, a thermometer and a dry-ice condenser. The mixture was purged 15 with nitrogen gas for one hour, and then the nitrogen purge was switched to a positive pressure nitrogen blanket. To the aqueous monomer emulsion were added 18.0 g of vinylidene chloride, 50.0 g acetone and 1.0 g 2,2'-azobis(2-amidinopropane) dihydrochloride dissolved in 10 g deionized water to initiate the polymerization. The resultant mixture was 20 heated to 50° C and held at 50° C for 8 hours. The polymerization yielded a polymer latex weighing 321 g with a solids content of 34.8%.

EXAMPLE 2

A water emulsion was prepared by mixing the following:

- 30.0 g of perfluoroalkylethyl acrylate mixture A
25 10.0 g of stearyl acrylate
 4.0 g of stearic acid/14-ethylene oxide adduct
 1.0 g of 2-hydroxyethyl methacrylate/9-ethylene oxide adduct
 0.15 g of ethoxylated carboxylated octadecylamine
30 0.5 g of N-methylolacrylamide
 0.5 g of 2-hydroxyethyl methacrylate
 0.25 g of dodecylmercaptan
 10.0 g hexylene glycol
 100.0 g deionized water.
35 The emulsion was added to a glass reaction vessel equipped with an agitator, a thermometer and a dry ice condenser. The mixture was purged with nitrogen gas for one hour, and then the nitrogen purge was switched

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to a positive pressure nitrogen blanket. To the aqueous monomer emulsion were added 10.0 g of vinylidene chloride and 0.5 g 2,2'-azobis(2-amidinopropane) dihydrochloride dissolved in 5.0 g deionized water to initiate the polymerization. The resultant mixture was heated to 50° C and held at 50° C for 8 hours. The polymerization yielded a polymer latex weighing 175 g with a solids content of 31.1%.

EXAMPLES 3-10 & CONTROLS A & B

Emulsion polymers were prepared substantially according to the procedure of Example 2 to provide the compositions given in Table 1.

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TABLE 1
Quantity of Monomers in Emulsion for Example/Control

	Monomer	(parts by weight)									
		3	4	5	6	7	8	9	10	A	B
	Perfluoroalkylethyl acrylate B	60	0	0	0	0	0	0	0	0	0
15	Perfluoroalkylethyl methacrylate A	0	60	0	0	0	0	0	0	0	0
	Perfluoroalkylethyl methacrylate B	0	0	60	60	80	50	60	60	60	60
20	2-Eethylhexyl methacrylate	20	0	20	0	0	0	0	0	0	0
	2-Eethylhexyl Acrylate	0	0	0	20	10	10	0	0	0	0
	Stearyl methacrylate	0	20	0	0	0	0	0	0	0	0
	Stearyl acrylate	0	0	0	0	0	0	0	20	40	0
25	Lauryl acrylate	0	0	0	0	0	0	20	0	0	0
	Vinylidene chloride	20	20	20	20	10	40	20	20	0	20
	N-methylolacrylamide	1	1	1	1	1	1	1	1	1	1
	2-Hydroxyethyl methacrylate	1	1	1	1	1	1	1	1	1	1
30	2-Hydroxyethyl methacrylate/ 2 10-Ethylene oxide adduct	2	2	0	0	0	2	2	2	0	0
	2-Hydroxyethyl methacrylate/ 0 7-Ethylene oxide adduct	0	0	2	2	2	0	0	0	0	2

TEST METHODS

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The following test methods were used to evaluate substrates treated with the fluoropolymers of EXAMPLES 1 - 10, CONTROLS A, B and other CONTROLS:

REPELLENCY TESTING

1. Fabric Treatment

A portion of the polymer dispersion was diluted with water to a polymer content of 0.5-2%, such that, after application to selected fabrics by padding, a fluorine level of 900-1200 ppm based on weight of fabric was obtained. The fabrics selected for testing included a blue nylon taffeta, a polyolefin nonwoven and undyed nylon and cotton upholstery fabrics. The polyolefin fabric was dried at room temperature for 24 hours and then heat-treated at 38°C for 10 seconds. The nylon taffeta fabric was air-dried for 24 hours and the upholstery fabrics were air-dried for 72 hours.

2. Water Repellency Spray Test

The treated fabric samples were tested for alcohol repellency using AATCC Standard Test Method No. 22 of the American Association of Textile Chemists and Colorists. In that test, 250 mL of water were poured in a narrow stream at a 27 degree angle onto a fabric sample stretched on a 6-inch (15.2 cm) diameter plastic hoop. The water was discharged from a funnel suspended six inches (15.2 cm) above the fabric sample. After removal of excess water, the fabric was visually scored by reference to published standards. A rating of 100 denotes no water penetration or surface adhesion; a rating of 90 denotes slight random sticking or wetting; lower values indicate greater wetting and a rating of 0 indicates complete wetting.

3. Water Repellency Test

A series of standard test solutions made from water and isopropyl alcohol (IPA) identified in Table 2 were applied dropwise to the fabric samples. Beginning with the lowest numbered test liquid (Repellency Rating No. 1) one drop (approximately 5mm in diameter or 0.05 mL volume) was placed on each of three locations at least 2 inches apart. The drops were observed for ten seconds. If after ten seconds two of the three drops were still visible as spherical to hemispherical, three drops of the next higher numbered test liquid were placed on adjacent sites and observed for ten seconds. This procedure was continued until one of the test liquids results in two of the three drops failing to remain spherical to hemispherical. The water repellency of the fabric was the highest numbered test liquid for which two of the three drops remained spherical to hemispherical.

TABLE 2
STANDARD WATER TEST SOLUTIONS

	Water Repellency	Composition		Water Repellency	Composition	
		Rating Number	% IPA	% Water	Rating Number	% IPA
5	1	2	98	7	50	50
	2	5	95	8	60	40
	3	10	90	9	70	30
	4	20	80	10	80	20
10	5	30	70	11	90	10
	6	40	60	12	100	0

4. Oil Repellency

Treated fabric samples were tested for oil repellency by a modification of AATCC Standard Test Method No. 118, conducted as follows. A series of organic liquids, identified below in Table 3 were applied dropwise to the fabric samples. Beginning with the lowest numbered test liquid, (Repellency Rating No. 1) one drop (approximately 5 mm in diameter or 0.05 mL volume) was placed on each of three locations at least 5 mm apart. The drops were observed for 30 seconds. If, at the end of this period, two of the three drops were still spherical to hemispherical in shape with no wicking around the drops, three drops of the next highest numbered liquid were placed on adjacent sites and similarly observed for 30 seconds. The procedure was continued until one of the test liquids results in two of the three drops failing to remain spherical to hemispherical, or wetting or wicking occurs. The oil-repellency rating of the fabric is the highest numbered test liquid for which two of the three drops remain spherical to hemispherical, with no wicking for 30 seconds.

TABLE 3
OIL REPELLENCY TEST LIQUIDS

	Oil Repellency Rating Number	Test Solution
	1	Nujol* Purified Mineral Oil (* Trademark of Plough, Inc.)
35	2	65/35 Nujol/n-hexadecane by volume
	3	n-hexadecane
	4	n-tetradecan

- 4 n-dodecane
6 n-decane

Using the foregoing three TEST METHODS to treat fabrics with the fluoropolymer compositions of EXAMPLES 1 - 10 and

5 CONTROLS A, B, C & D (described below), all in the form of aqueous emulsions, showed that the fluoro-polymers of EXAMPLES 1 - 10 imparted oil- and water-repellency to the fabrics tested without the need to effect curing at elevated temperature by prior art procedures, whereas the CONTROL polymers either failed to do so at all or did so to an extent

10 which would not be suitable commercially. CONTROL A contained no polymer units derived from vinylidene chloride. CONTROL B contained no polymer units derived from a nonfluorinated (meth)acrylate.

CONTROL C consists of an aqueous emulsion copolymer of 60% perfluoroalkylethyl acrylate, 20% stearyl acrylate, 20% vinylidene

15 chloride, 1% each N-methylolacrylamide, 2-hydroxyethyl methacrylate and 2% 2-hydroxyethyl methacrylate/ethylene oxide (6) adduct. The perfluoroalkylethyl acrylate used to produce the CONTROL C finish was a mixture of monomers characterized by the general formula:

20 $\text{CF}_3\text{CF}_2(\text{CF}_2)_k\text{C}_2\text{H}_4\text{OC(O)CH}=\text{CH}_2$
wherein k = 4, 6, 8, 10, and >12 as described by Greenwood, et al. (vide supra). CONTROL D is a commercial repellent product for textiles derived from a physical blend described in U.S. Pat. No. 4,595,518 which is based on:

25 1. A Perfluoroalkylethyl citrate urethane (anionic dispersion);
2. A 75/25/0.25/0.25 perfluoroalkylethyl methacrylate/2-ethylhexylmethacrylate/N-methylol-acrylamide/2-hydroxyethyl methacrylate copolymer;

30 3. A 65/35/0.25 perfluoroalkylethyl methacrylate/Lauryl methacrylate/N-methylolacrylamide copolymer and
4. Neoprene Latex, dispersed with Tween 80 surfactant, and the pH adjusted with polydimethylaminoethyl-methacrylate/acrylics.

CLAIMS

1. A copolymer the polymer units of which consist essentially of

- 5 a) 50-80 weight.% of perfluoroalkylethyl (meth)acrylates,
- b) 10-40 weight.% of a C₂-C₂₀ alkyl (meth)acrylate,
- c) 10-40 weight.% of vinylidene chloride,
- d) 0-2 weight.% of N-methylol-acrylamide,
- e) 0-2 weight.% of 2-hydroxyethyl methacrylate and
- 10 f) 0-5 weight.% of 2-hydroxyethyl methacrylate/ethylene oxide adduct;

said perfluoroalkyl-ethyl (meth)acrylates being in the form of mixtures of monomers having the formula:



15 wherein R = H or CH₃, and k is 4,6,8,10 and 12 having a distribution consisting essentially of:

25-70 weight % of monomers wherein k = 4 or less

20-40 weight % of monomers wherein k = 6

5-25 weight % of monomers wherein k = 8

20 0-15 weight % of monomers wherein k = 10 or greater.

2. The polymer of Claim 1 wherein said

fluoro(meth)acrylate monomer distribution consists essentially of:

45-70 weight % of monomers wherein k = 4 or less

20-35 weight % of monomers wherein k = 6

25 5-10 weight % of monomers wherein k = 8

0-5 weight % of monomers wherein k = 10 or greater.

3. The polymer of Claim 1 wherein said

fluoro(meth)acrylate monomer distribution consists essentially of:

25-45 weight % of monomers wherein k = 4 or less

30 25-40 weight % of monomers wherein k = 6

10-25 weight % of monomers wherein k = 8

1-15 weight % of monomers wherein k = 10 or greater.

4. The polymer of Claim 1 wherein R is CH₃.

35 5. A process for imparting oil- and water-repellency to a fibrous substrate which consists essentially in applying to said substrate an aqueous emulsion of the polymer of either Claim 1, 2, 3 or 4, and drying the so-treated substrate.

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/US 94/03434

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08F220/22 D06M15/277

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08F D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 234 724 (E.I.DU PONT DE NEMOURS AND CO.) 2 September 1987 cited in the application -----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

9 August 1994

Date of mailing of the international search report

02.09.94

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/03434

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0234724	02-09-87	US-A- 4742140	03-05-88
		AU-B- 600924	30-08-90
		AU-A- 6792087	30-07-87
		CA-A- 1271892	17-07-90
		FI-B- 89374	15-06-93
		JP-A- 62179517	06-08-87